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13. ABSTRACT (Maximum 200 words) Because of the importance of this starting material, considerable effort was expended on modification of the reported workup. Elimination of all extraction and careful acidification of the diluted reaction mixture at low temperature leads to a consistent 40-50% yield of product exhibiting the characteristics of previously prepared samples. In addition to our interest in this material it appears to be an important starting material for the synthesis of anthracene intermediates. Anthracenes are used as antitumor antibiotics(c.f., Henry, D.W., Cancer.Treat.Rep 1979, 63, 845) in which they act as DNA intercalators. A publication specifying the details of the synthesis and workup is being prepared.					
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FINAL TECHNICAL REPORT

Single Lithium Ion Conducting Polymer Electrolyte

AFOSR - F49620-97-1-0169

1 May, 1997 - 30 April, 1998

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Preface

The effort on this project began on May 1, 1997 and continued, through an extension from NCEE and the Department of Chemistry, Wright State University, until May 31, 1998

1. Naphthacene Synthesis

Proposed Synthesis

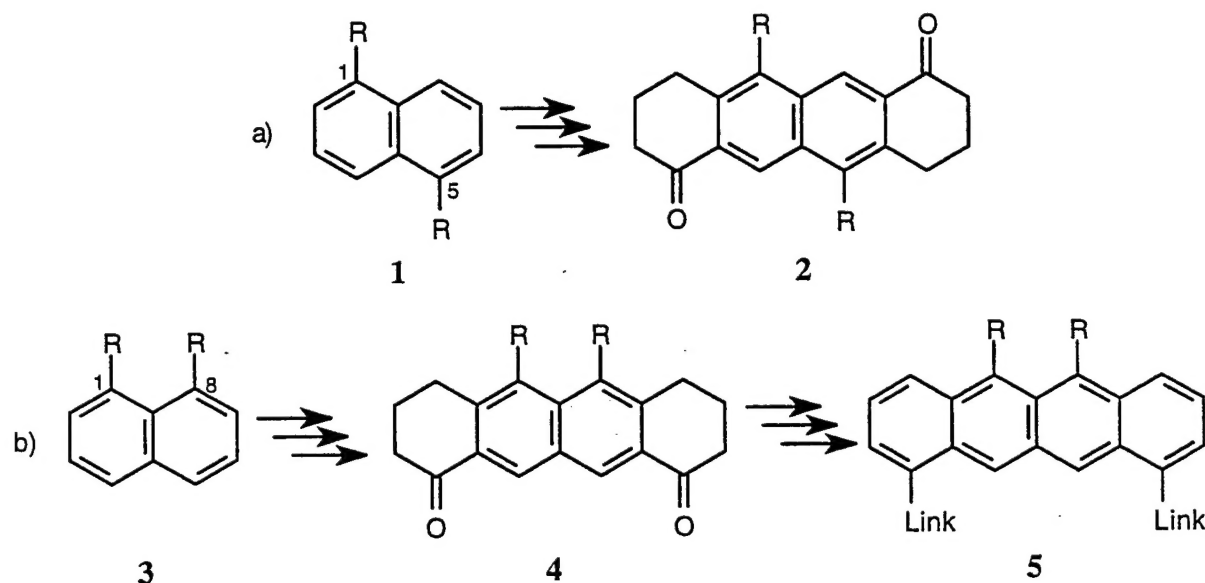
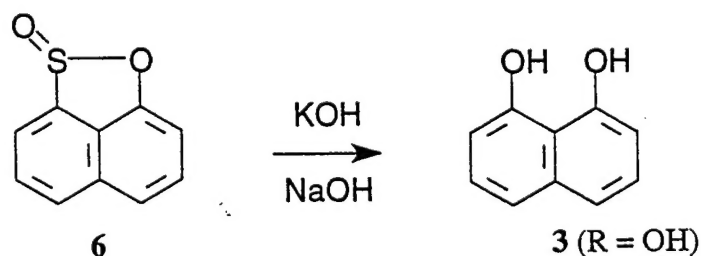


Figure 1. a) The reported synthesis of a 1,5-disubstituted naphthacene precursor, b) The proposed regiospecific double annulation synthesis of the 1,10-disubstituted naphthacene spacer unit.

As outlined in the original proposal (Appendix A), the successful synthesis of arrangements of two, or more, porphyrins pillared by a naphthacene spacer in a cofacial arrangement was crucial. Initially, a template of the reported conversion of 1 ($R = OH$), which is commercially available, to the diketone 2 ($R = OCH_3$) involving seven (7) steps and in 58% yield considered. The proposed regiospecific double annulation synthesis of 4 ($R = OCH_3$), would involve eight (8) steps, one of which is the synthesis of 3 ($R = OH$).

1,8-Dihydroxynaphthalene



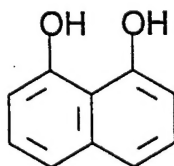
The synthesis of 3 has been reported to involve the fusion of the sultone 6 with a mixture of sodium and potassium hydroxide [a) N.G. Anderson, S.P. Maddaford and B.A. Keay, *J.Org.Chem.*, **1996**, *61*, 9556, b) A.P. Lurie, G.H. Brown, J.R. Thirtle and A.J. Weissberger, *J.Am.Chem.Soc.*, **1961**, *83*, 5015, F. Hibbert and K. Spears, *J.Chem.Soc., Perkin Trans. 2*, **1988**, 571, N.G. Anderson, *personal communication*.]. The workup of the reaction mixture involved acidification followed by a series of tedious and expensive extractions.

Achievement

Because of the importance of this starting material, considerable effort was expended on modification of the reported workup. Elimination of all extraction and careful acidification of the diluted reaction mixture at low temperature leads to a consistent 40-50% yield of product exhibiting the characteristics of previously prepared samples. In addition to our interest in this material it appears to be an important starting material for the synthesis of anthracycline intermediates. Anthracyclines are used as antitumor antibiotics (c.f., Henry, D.W., *Cancer.Treat.Rep.* **1979**, *63*, 845) in which they act as DNA intercalators. A publication specifying the details of the synthesis and workup is being prepared.

EXPERIMENTAL

Improved Synthesis of 1,8-Dihydroxynaphthalene

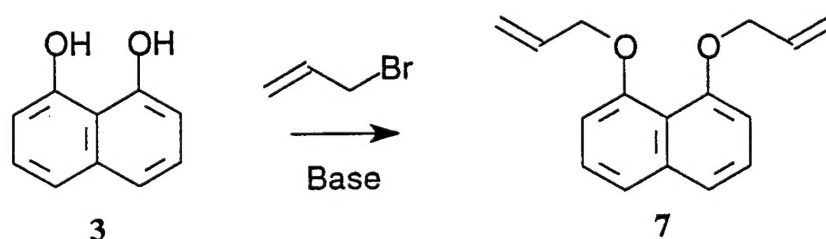


A mixture of 100g NaOH, 100g KOH and 15g of naphthosultone was placed in a 2L stainless steel beaker equipped with a stainless steel cover, a thermometer well, a nitrogen inlet and a

vapor exit. The reactor was heated to 230°C for 45 min. The reaction mixture was then cooled in an ice-bath to cause immediate solidification. The brown solid was crushed and dissolved in water (400 mL). The resulting basic solution was carefully acidified (pH 2) with concentrated HCl, boiled for 30 min, filtered hot and cooled in an ice-bath. The off-white product (10.5g, 42%) precipitates from solution and can be recrystallized from CH₂Cl₂/hexanes: mp 141-3°C.

1,8-Bisallyloxynaphthalene

The second step in the synthesis of a 1,10-disubstituted naphthacene system was the reaction of 1,8-dihydroxynaphthalene (**3**) with allyl bromide to yield 1,8-bisallyloxynaphthalene (**7**). The



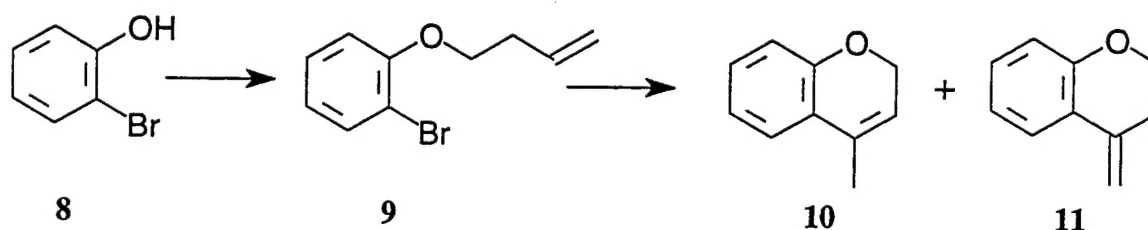
synthesis of the **7** has proven to be insurmountable under this contract. Unforeseen steric and/or electronic effects are apparently precluding a successful synthesis. Various attempts and methods have been explored in order to obtain this product cleanly and in reasonable yield, i.e. devoid of the half-product, 8-allyloxy-1-naphthol in yields over 10-20%. The following synthetic methods have been examined:

- 1,8-dihydroxynaphthalene was reacted with K₂CO₃ and allyl bromide in refluxing acetone (Takahashi, et.al., *Syn. Comm.*, **1990**, 20. 1569).
- 1,8-dihydroxynaphthalene was reacted with K₂CO₃ and allyl bromide in DMF.
- 1,8-dihydroxynaphthalene was reacted with NaH in ether to preform the dialkoxide followed by reaction with allyl bromide.
- 1,8-dihydroxynaphthlene was reacted with NaH in 1,2-dimethoxyethane (MG) followed by reaction with allyl bromide.

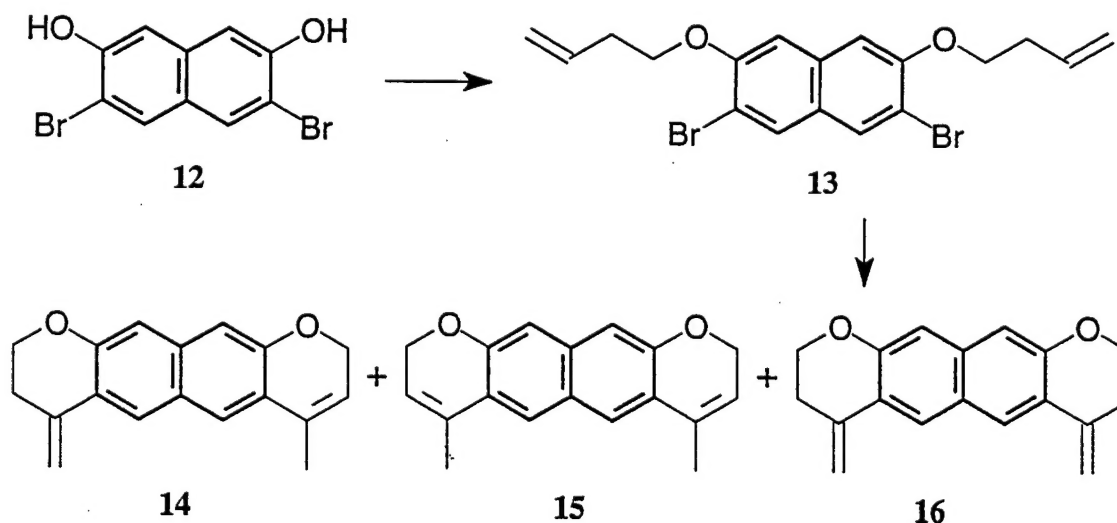
Further progress in the synthesis of a 1,10-disubstituted naphthacene pillared porphyrin linking unit is dependent on a successful synthesis of 1,8-bisallyloxynaphthalene.

2. Naphthacene Related Synthesis

An alternative to the all-aromatic naphthacene pillar was envisioned to be accessible by way of the palladium-catalyzed cyclization of 1-(4-butenyloxy)-2-bromobenzene (**9**) that was prepared from the corresponding phenol, o-bromophenol (**8**). A mixture of products was formed (**10** and **11**) that have appropriate functionality for further elaboration. The availability of

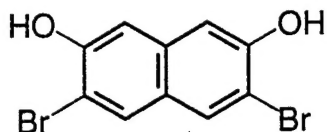


3,6-dibromo-2,7-dihydroxynaphthalene (**12**) from a previous study was used as a starting point for the synthesis of the corresponding bis(4-butenyl) ether **13**. Complete characterization of **13** was not accomplished and its conversion to a mixture of **14**, **15** and **16** was therefore not undertaken. Compounds **14**, **15** and **16** all contain functionality correctly spaced for use as an alternative to the naphthacene pillar **5**.



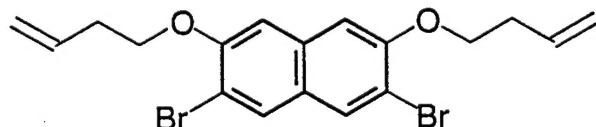
EXPERIMENTAL

3,6-Dibromo-2,7-dihydroxynaphthalene



A literature procedure was used to prepare 3,6-dibromo-2,7-dihydroxynaphthalene (Cooke, R.G., Johnson, B.L. and Owen, W.R., *Aust.J.Chem.*, **1960**, 256). Bromine (26 g) in acetic acid (50 mL) was added slowly to 2,7-dihydroxynaphthalene (6.5 g) in acetic acid (150 mL). The mixture was diluted with 20 mL of water and refluxed while 10 g of tin was added. Heating was continued for 4 h and the solution was cooled to 50°C and filtered. The precipitated product was recrystallized from acetic acid to give 10.5 g (86%) of 3,6-dibromo-2,7-dihydroxynaphthalene: m.p. 188-189.

3,6-Dibromo-2,7-bis(3-butenoxy)naphthalene

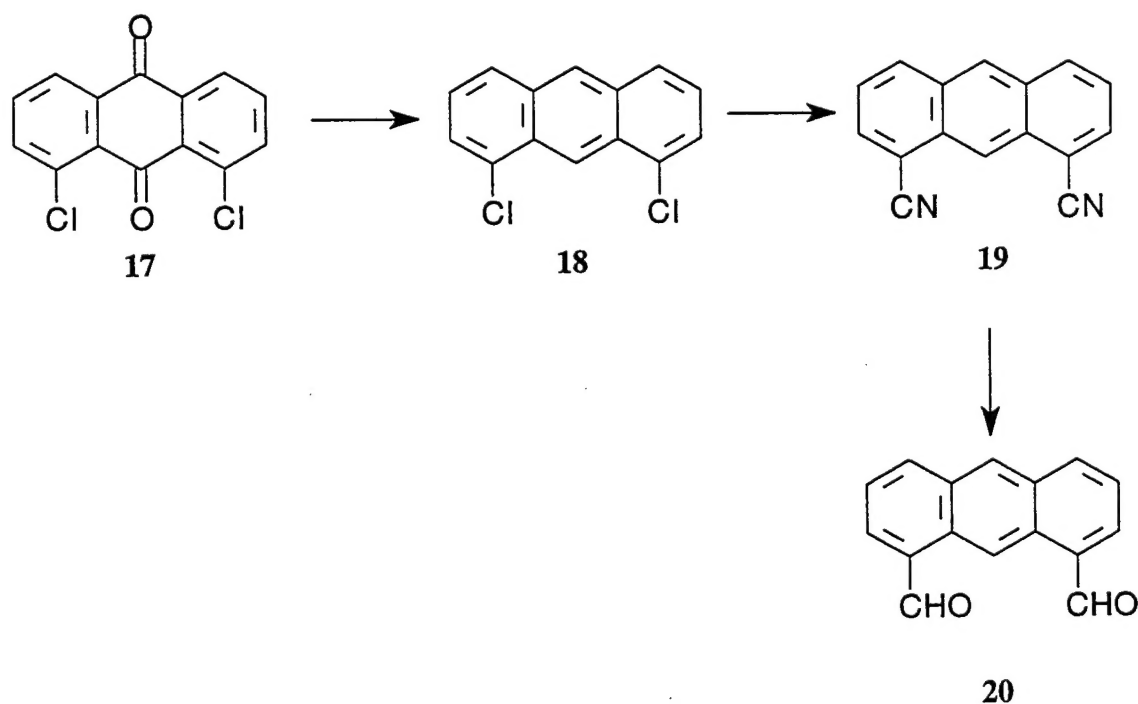


The bisallyl ether derivative of 3,6-dibromo-2,7-dihydroxynaphthalene was prepared by analogy to the procedure of Shi, et.al. (Shi, L., et.al., *J.Am.Chem.Soc.*, **1983**, 48, 3895). The reaction of 3,6-dibromo-2,7-dihydroxynaphthalene with 2 equivalents of 4-bromo-1-butene in acetone was carried out in the presence of excess potassium carbonate. The reaction mixture was refluxed for 72 h. The acetone was removed and water was added to the residue. The aqueous layer was extracted with ether and the ether layers combined and washed with 10% NaOH. The organic layer was dried, filtered and evaporated. This compound was not fully characterized.

2. 1,8-DiformylAnthracene Synthesis

The synthesis of arrangements of two, or more, porphyrins pillared by an anthracene spacer in a cofacial arrangement has been reported [a) I. Abdalmuhdi and C.K. Chang, *J.Org.Chem.*, **1985**, *50*, 411, b) T. Nagata, A. Osuka and K. Maruyama, *J.Am.Chem.Soc.*, **1989**, *112*, 3054.]. The synthesis of the anthracene pillar, 1,8-diformylanthracene (**20**), was undertaken to provide a comparison of the anthracene and naphthacene pillars with respect to the porphyrin spacing in both a mono and di-lithium form.

The synthesis 1,8-dichloroanthracene (**18**) was accomplished by the reduction/dehydration of 1,8-dichloroanthraquinone (**17**) with zinc in aqueous ammonia followed by HCl/ethanol.



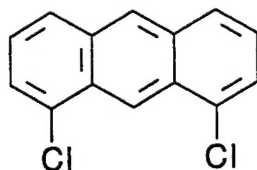
Replacement of the halogens of **18** with cyano functions was carried out using cuprous cyanide.

Reduction of the dicyano compound **19** with DIBAL-H provides 1,8-diformylanthracene (**20**).

Elaboration of the aldehyde functions into porphyrin rings was not carried out.

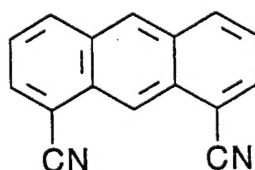
EXPERIMENTAL

1,8-Dichloroanthracene



The compound 1,8-dichloroanthracene was prepared as reported (Golden, R. and Stock, L.M., *J. Am. Chem. Soc.*, **1971**, *94*, 3080). A 5L flask was charged with 80g (0.288 mole) of 1,8-dichloroanthraquinone and 3L aqueous ammonia. As the mixture was stirred, 320g (4.9 mole) zinc dust and 1.5g cupric sulfate were added over a few min. The mixture was gently heated for 90 min. The temperature of the solution was then raised to 80°C and it was stirred for 4.5h. The hot mixture was filtered and yielded a gray solid that was washed with and extracted with three portions of acetone, which were combined and evaporated. The resulting solid was dissolved in hot propanol and HCl was added dropwise until crystals began to appear. The yellow needles were washed with cold methanol to yield 69 g (94%) of 1,8-dichloroanthracene: m.p. 157-158 C.

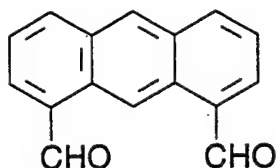
1,8-Dicyanoanthracene



A literature procedure was used to prepare 1,8-dicyanoanthracene (Guilard, R., et.al., *J. Am. Chem. Soc.*, **1992**, *114*, 9877). A 1L, three-necked flask was charged with 1,8-dichloroanthracene (46.2 g, 0.19 mole), cuprous cyanide (60g) and 500 mL of freshly distilled N-methylpyrrolidinone. The mixture was refluxed under nitrogen. After 24 hours more cuprous cyanide (10g) was added. The reaction was followed by TLC. After a total of 4 days the reaction was complete. The mixture was cooled and poured into 1L of water. One liter of aqueous

ammonia was added and the mixture was stirred for 4 days. The resulting brown precipitate was filtered and washed with water. The solid was added to 200 ml of aqueous ammonia, filtered and washed with water. Recrystallization from dimethylformamide (3L) gave 32 g (73%) 1,8-dicyanoanthracene: m.p. 301-303.

1,8-Diformylanthracene



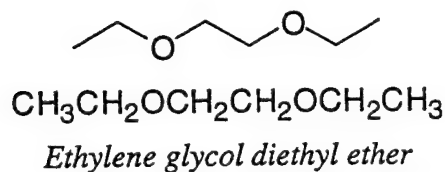
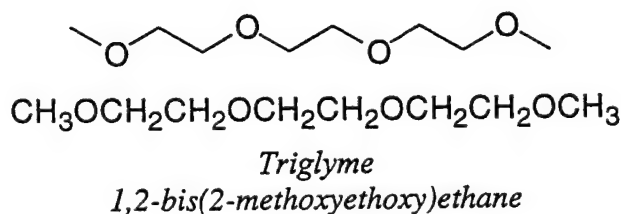
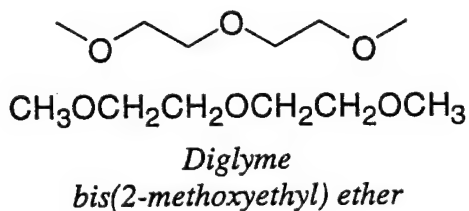
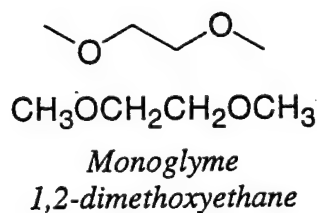
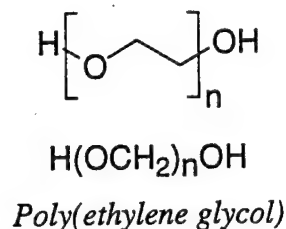
A literature procedure was used to prepare 1,8-diformylanthracene (*J. Am. Chem. Soc.*, 1992, 114, 9877). A suspension of 1,8-dicyanoanthracene (10 g, 43.9 mmol) in 425 mL of dry methylene chloride was cooled to 0 °C and diisobutylaluminum hydride (DIBAL-H) (88 mL, 1 M solution) was rapidly added. An additional 40 mL of DIBAL-H was added after 15 minutes. The mixture was stirred at 0 °C for 15 min and then at room temperature for 30 min. The solution was poured into aqueous sulfuric acid (60%, 350 mL) at 0 °C. The mixture was diluted with water (4 L) and the water layer extracted with methylene chloride. The organic extracts were combined, dried (MgSO₄), filtered and evaporated. Recrystallization of the resulting solid from ethanol gave 4.1 g (40%) of 1,8-diformylanthracene: m.p. 187-8 °C.

4. Poly(ethylene oxide) Model Compound Decomposition Study (GC/MS)

The objective of this study was to investigate the decomposition of the poly(ethylene oxide) model compounds ethylene glycol dimethyl ether (1,2-dimethoxyethane, monoglyme), diethylethylene glycol dimethyl ether (bis(2-methoxyethyl) ether, diglyme), triethylene glycol

dimethyl ether (1,2-bis(2-methoxyethoxy)ethane, triglyme) and ethylene glycol diethyl ether.

Each compound was brought in contact with Na/NaI or Li/LiI at room temperature.



Experimental Conditions and Instrumentation: The reactions were carried out on 1 M solutions in septum sealed vials. In the case of monoglyme, diglyme, and diethyethylene glycol, the reactions were carried out on a 5 mmole scale. The reactions of triglyme were carried out on a 3 mmole scale. Head-space vapor analysis was carried out using a Supelco Manual Solid Phase Micro-Extraction Holder (Supelco 5-7330) with a Supelco non-polar fiber (Supelco 57300-U). The GC-MS employed was a Hewlett-Packard Model 6890 GC with a Model 5973 MS Detector. The program utilized for analysis was VOC_5M, which holds the initial temperature at 35°C for 5 minutes followed by an increase of 25°C/min. The extract ions used in the study were 15, 29, 31, 45 and 46. These ions were extracted from the spectrum and integrated. Calibration curves for methanol and ethanol was obtained for 10,000 ppm, 1000 ppm, 100 ppm and 50 ppm. The

hydrolysis reaction was performed by removing 0.1 mL of the reaction mixture *via* syringe and placing the mixture in a 1 mL vial. A small amount of water was added (10 drops) to the mixture. Prior to analysis by GC-MS the fiber was placed in the vapor space of the vial for 20-30 minutes. The fiber was then removed and inserted into the MS. The fiber was allowed to remain in the injection port for 1 minute to desorb the materials.

Monoglyme

Analysis of the monoglyme **blank** reaction (no metal or metal salts) over a period of time indicated that **no** production of **methanol** was observed. In the analysis, the production of methanol is indicated by a change in the ratio of the 15, 29 and 31 mass ions – none was observed in this case. Analysis of the reaction of **Na/NaI** in the presence of monoglyme showed **no** indication of **methanol** production. The ratio in the Na/NaI stayed the same. Analysis of the reaction mixture of **Li/LiI** in the presence of monoglyme indicated that after hydrolysis **methanol was present** and, in addition, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ (methoxyethanol). It should be noted that when the LiI was added to the vial containing the Li metal and monoglyme, an exothermic reaction was observed. This did not occur in the analogous Na/NaI reaction. However, in both the Na/NaI and Li/LiI reactions the presence of a solid was noted. The entire reaction mixture was hydrolyzed and analysis of the solution confirmed the presence of methanol and methoxyethanol.

Diglyme

Analysis of the diglyme **blank** reaction (no metal or metal salts) over a period of time indicated that **no** production of **methanol** was observed (by monitoring the 15, 29 and 31 mass ions as before). Analysis of the reaction of Na/NaI in the presence of diglyme showed no indication of **methanol** production. Analysis of the reaction mixture of **Li/LiI** in the presence of

diglyme indicated that after hydrolysis **methanol** was present and, in addition, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ (methoxyethanol). It should be noted that when the LiI was added to the vial containing the Li metal and diglyme, an exothermic reaction was observed. This did not occur in the analogous Na/NaI reaction. However, in both the Na/NaI and Li/LiI reactions the presence of a solid was noted. The entire reaction mixture was hydrolyzed and analysis of the solution confirmed the presence of methanol and methoxyethanol

Triglyme

Analysis of the triglyme **blank** reaction (no metal or metal salts) over a period of time indicated that **no** production of **methanol** was observed (by monitoring the 15, 29 and 31 mass ions as before). Analysis of the reaction of Na/NaI in the presence of triglyme showed **no** indication of **methanol** production. Analysis of the reaction mixture of **Li/LiI** in the presence of triglyme indicated that after hydrolysis **methanol** was present along with $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ (2-methoxyethanol), $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (triethylene glycol) and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (2-(2-methoxyethoxy)ethanol). It should also be noted that when the LiI was added to the vial containing the Li metal and triglyme, an exothermic reaction was observed. This did not occur in the analogous Na/NaI reaction. However, in both the Na/NaI and Li/LiI reactions the presence of a solid was noted. The entire reaction mixture was hydrolyzed and analysis of the confirmed the presence of methanol, 2-methoxyethanol, triethylene glycol and 2-(2-methoxyethoxy)ethanol.

Ethylene Glycol Diethyl Ether

Analysis of the ethylene glycol diethyl ether **blank** reaction (no metal or metal salts) over a period of time indicated **no** production of **ethanol** was observed (by monitoring, in this case, the 15, 45 and 46 mass ion ratio). Analysis of the reaction of Na/NaI in the presence of ethylene

glycol diethyl ether showed no indication of ethanol production. Analysis of the reaction mixture of **Li/LiI** in the presence of ethylene glycol diethyl ether indicated that after hydrolysis, **ethanol** was present as well as $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (2-ethoxyethanol). It should also be noted that when the LiI was added to the vial containing the Li metal and ethylene glycol diethyl ether, an exothermic reaction was observed. This did not occur in the analogous Na/NaI reaction. However, in both the Na/NaI and Li/LiI reactions the presence of a solid was noted. The entire reaction mixture was hydrolyzed and analysis of the confirmed the presence of ethanol and 2-ethoxyethanol.

Summary of Poly(ethylene oxide) Model Compound Decomposition Study (GC/MS)

	Monoglyme	Diglyme	Triglyme	Ethylene Glycol diethyl Ether
<i>Blank</i>	<i>No Methanol</i>	<i>No Methanol</i>	<i>No Methanol</i>	<i>No Ethanol</i>
Na/NaI	<i>No Methanol</i>	<i>No Methanol</i>	<i>No Methanol</i>	<i>No Ethanol</i>
Li/LiI	<i>Methanol 2-Methoxyethanol</i>	<i>Methanol 2-Methoxyethanol</i>	<i>Methanol 2-Methoxyethanol</i>	<i>Ethanol 2-(2-methoxyethoxy)ethanol Triethylene glycol</i>
Comment	<i>Li/LiI exothermic. Solid present in both Na and Li reactions.</i>	<i>Li/LiI exothermic Solid present in both Na and Li reactions.</i>	<i>Li/LiI exothermic Solid present in both Na and Li reactions.</i>	<i>Li/LiI exothermic Solid present in both Na and Li reactions.</i>

Achievement

The fragmentation of poly(ethylene oxide) model compounds in the presence of Li/LiI but not in the presence of Na/NaI has been demonstrated at room temperature. These results confirm previous calculations concerning the mode of performance degradation in lithium ion batteries. Publication of these results is in progress.

Appendix A. Original Proposal

Single Lithium Ion Conducting Polymer Electrolyte

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Introduction

The need for power storage systems that are compact and have both high power and high energy density has become acute for diverse reasons. Military and commercial requirements are similar and include high-efficiency, lightweight, nonpolluting (in both manufacture and disposal) systems that overcome the limitations of current and previous designs. A recent article¹ addresses new developments in the battery technology area and indicates that "the number of practical applications for electrochemical power sources has increased dramatically, so that what was seen up to the 1980s as a relatively mature industry, has now become one with significant growth." The range of applications that is driving this growth includes 'smart' cards, electric watches, calculators, portable computers, mobile phones, pagers and electric vehicles in the commercial/consumer arena and mobile/fixed communication, missile guidance systems, and satellite or space vehicle power/communication/guidance, in the military arena.

Rapid advances and application of lithium battery technology have placed these systems at the forefront of current research and development. Typical polymer electrolytes used in the current generation of lithium batteries use oxygen-containing materials as electrolytes and are dual ion conductors. This type of electrolyte relies heavily on polymer segmental motion to allow the ionic conduction required for battery performance. Due to the physical nature of these oxygen-based materials, their segmental motion is severely restricted at ambient and subambient temperatures - exactly those temperatures at which both military and commercial/consumer high performance is required. In addition, the dual ion conducting polymer electrolyte can suffer from voltage losses across the electrolyte under high pulse power conditions because of a buildup of a

cation/anion concentration gradient. The need exists, therefore, for the development of a totally new polymer electrolyte wherein there is a radical change in the ionic conduction mechanism that 1) eliminates the dependency on polymer segmental motion and 2) is a single lithium ion conductor. The following section describes the structure of an electrolyte that can satisfy these requirements.

Project Description

Computational chemistry has been used by Wright Laboratory (POOB) to design a lithium ion conducting polymer electrolyte channel that would eliminate the polymer segmental motion based ionic conduction mechanism. Thus it would have a low energy of activation and perform well at subambient temperatures. The basis for the design is the generation of a constant-solvation sphere for the lithium ion whereby the lithium ions experience a constant electrostatic potential throughout the channel. The formation of this channel can be accomplished through proper spacing of an unsaturated macrocyclic compound such as a dilithium porphyrin. Ionic conduction is based upon the potential difference created by the electrodes of the cell as well as lithium-ion/lithium-ion repulsion within the channel. It is anticipated that the energy of activation associated with ionic motion in the channel system would be about 0.2 eV as compared to 1.0-1.5 eV for current generation solid polymer electrolytes. This estimate is based on the results obtained from the study² of layered nanocomposite polymer electrolytes where there is dispersed negative charge throughout the system. The channel would also allow efficient operation at subambient temperatures due to the fact that once the channels are established, no further molecular motion is required for ionic conduction to occur. In addition, computational results indicate that the new electrolyte should be stable at the lithium anode. As stated earlier, the crucial factor in the establishment of channels is the spacing of the porphyrin channel units. This is shown schematically in Figure 1. The synthesis of arrangements of two, or more, porphyrins pillared by an anthracene spacer in a cofacial arrangement has been reported³ as a model for the study of the dynamics of energy transfer without

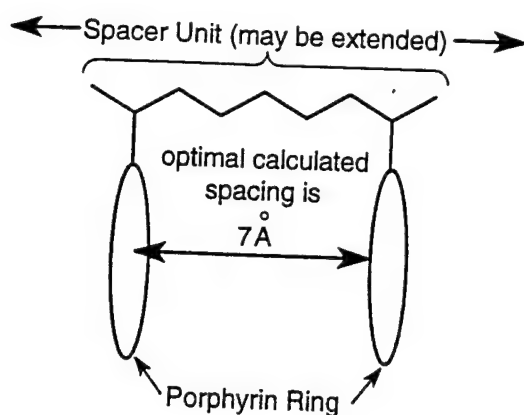


Figure 1. Schematic of computational design of porphyrin channel ionic conductor.

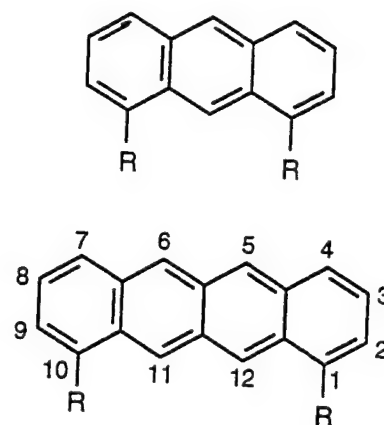


Figure 2. The anthracene (upper) and naphthalene (lower) spacer units with required disubstitution patterns.

complications of conformational motions. The current proposal addresses the required 7 Å spacing of porphyrins for optimum ion channel construction.

The proposed research will involve; 1) the generation/synthesis of the appropriate spacer, 2) the electrochemical characterization of the spacer unit, 3) the attachment of appropriate porphyrin channel units, 4) the electrochemical characterization of the combined spacer/porphyrin subsystems, 5) alignment studies of subsystems to determine their propensity to form extended, ordered porphyrin arrays, and 6) the optimization of the spacer length and characterization of an improved spacer by an iterative process employing steps 1-6.

As shown in Figure 1, computational studies indicated the optimum interchannel unit separation to be about 7 Å. The spacer unit that corresponds to such a spacing is the 1,10-disubstituted naphthalene nucleus as shown in Figure 2. The synthesis of 1,10-disubstituted naphthalenes is not addressed directly in the literature.

Preliminary investigation of the synthesis of a 1,10-disubstituted naphthalene by a Diels-Alder cycloaddition involving a bisbenzyne⁴ (Figure 3) indicated that the inherent generation of isomers and their separation makes this method of little use in a 1,10-disubstituted naphthalene synthesis.

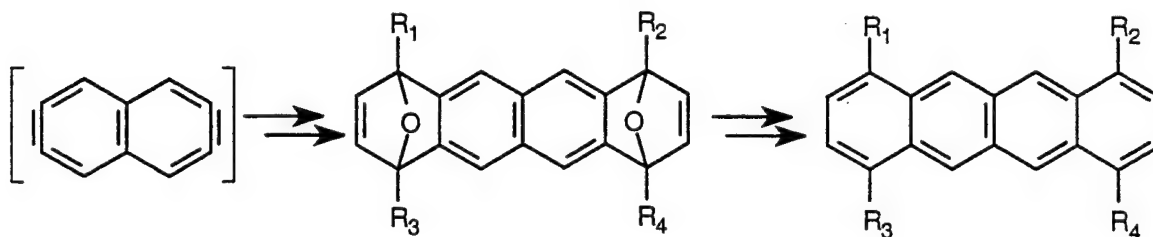


Figure 3. The bisbenzyne approach is not useful because of isomers which in one case (desired) have $R_1 = R_2 = H$ and $R_3 = R_4 = CHO$ and in the other (undesired) have $R_1 = R_4 = H$ and $R_2 = R_3 = CHO$.

The synthesis of a 1,10-disubstituted naphthacene by a series of steps outlined in Figure 4b is currently under consideration. This synthesis is analogous to that reported for an isomeric system as shown in Figure 4a.⁵ The availability of 1,8-dihydroxynaphthalene (Figure 4b starting material) has recently been addressed.⁶ In this context, the R groups act as directors and as place holders during the synthesis. The naphthacene spacer unit must be inert to the conditions encountered during subsequent synthetic procedures as well as during its lifetime in the electrochemical cell. The stability of the spacer unit, and in particular the influence of the R groups, will be investigated.

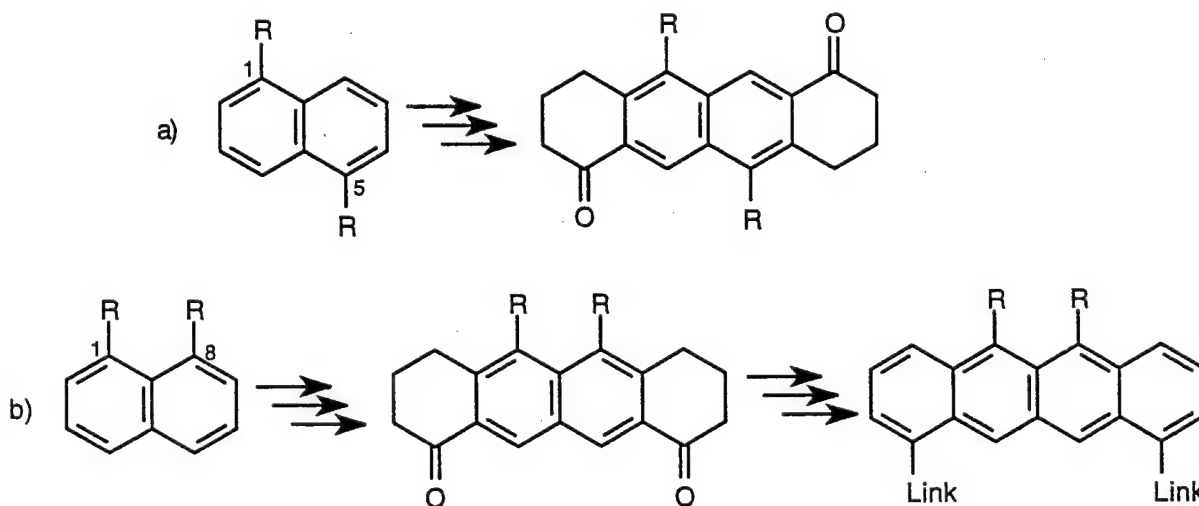


Figure 4. a) The reported synthesis of a 1,5-disubstituted naphthacene precursor, b) The proposed regiospecific double annulation synthesis of the 1,10-disubstituted naphthacene spacer unit.

A recent report⁷ delineated the use of the cholic acid subsystem as a spacer unit for the construction of a "molecular tweezers." This is of particular interest in this proposal because 1) the separation dimensions are approximately the desired ones, 2) the saturated frame of the steroidal backbone would not be expected to be electrochemically active, and 3) the basic unit is available naturally. We propose to investigate this subsystem in tandem with the aforementioned naphthacene system.

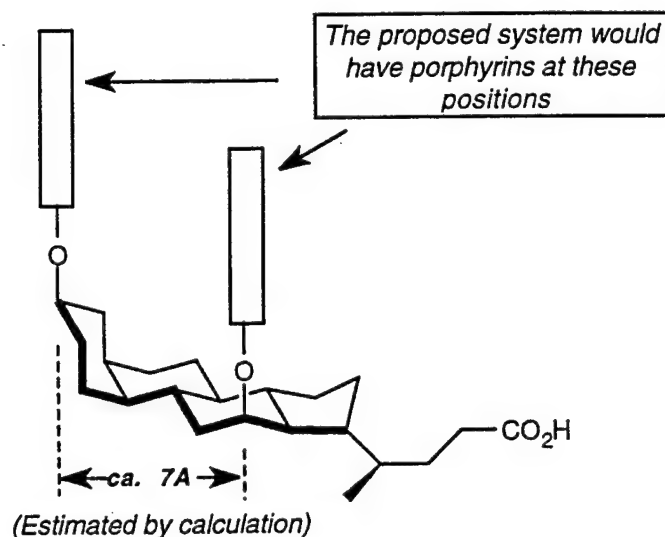


Figure 5. Cholic acid based spacer unit dimensional characteristics.

The construction of porphyrin subunits and arrays has been, and continues to be, addressed extensively in the literature^{3,8} due to the importance of such arrays in the photosynthetic process. These are, however, hydrogen-based porphyrin arrays only. These reports describe ribbons, ladders, pillared, dendritic, linear and planar porphyrin array synthesis and characterization. An important result of these studies is the finding, by NMR, that the porphyrin rings can be aligned. In addition, the synthesis of new subunits and the improvement of synthetic methods for existing subunits as well as the development of new porphyrin assembly techniques makes it likely that the synthesis and characterization of an appropriate spacer can be followed closely by the generation of a model channel porphyrin array having the computationally designed spacing.

Electrochemical characterization of the channel array will suggest future improvements and new synthetic objectives.

References

1. C.A. Vincent, "Recent Developments in Battery Technology," *Chemistry & Industry*, September 16, **1996**.
2. W. Krawiec, L.G. Scanlon, J.P. Fellner, R.A. Vaia, S. Vasudevan, E.P. Giannelis, *J. Power Sources*, **1995**, *54*, 310.
3. a) I. Abdalmuhdi and C.K. Chang, *J.Org.Chem.*, **1985**, *50*, 411, b) T. Nagata, A. Osuka and K. Maruyama, *J.Am.Chem.Soc.*, **1989**, *112*, 3054.
4. G.W. Gribble, R.B. Perni and K.D. Onan, *J.Org.Chem.*, **1985**, *50*, 2934.
5. I. Takahashi, A. Nomura and H. Kitajima, *Synth.Comm.*, **1990**, *20(10)*, 1569.
6. a) N.G. Anderson, S.P. Maddaford and B.A. Keay, *J.Org.Chem.*, **1996**, *61*, 9556, b) A.P. Lurie, G.H. Brown, J.R. Thirtle and A.J. Weissberger, *J.Am.Chem.Soc.*, **1961**, *83*, 5015, F. Hibbert and K. Spears, *J.Chem.Soc., Perkin Trans. 2*, **1988**, 571, N.G. Anderson, *personal communication*.
7. L. D'Souza and Uday Maitra, *J.Org.Chem.*, **1996**, *61*, 9494.
8. D.L. Officer, A.K. Burrell and D.C.W. Reid, *Chem.Comm.*, **1996**, 1657 and references cited therein.

Appendix B. Ventura AFOSR/ONR Review Slides

Single Lithium Ion Conducting Polymer Electrolyte

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Wright State University
Dayton, OH 45435

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AFOSR/CA V98.1

Lithium Power Storage Systems

- High-power and high-energy-density
 - high-efficiency
 - lightweight
 - non-polluting
- Applications have increased
 - commercial/consumer
 - military

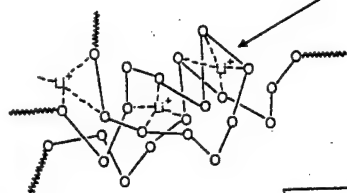
"Rechargeable lithium batteries," *Chemical Society Reviews*, 1997, 26, 259

AFOSR/CA V98.2

Current Electrolytes

PEO based electrolytes

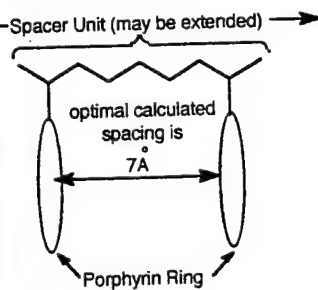
Movement of Li^+
requires chain
segments to move



New conduction pathway

AFOSR/CA V98 3

Computational Channel Design



Channel Concept
low activation energy
low temp. activity

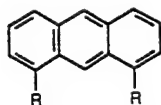
$E_{act} = 0.2 \text{ eV (calc.)}$
 $1.0 - 1.5 \text{ eV (current)}$

"Porphyrin Spacing"

"Escorting Metal Ions," C&EN, November 10, 1997
"Nanotube Characterization," C&EN, January 5, 1998

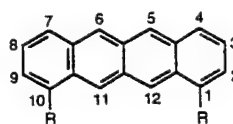
AFOSR/CA V98 4

Pillared Porphyrins



Cofacial anthracene pillar

- provided information on energy transfer without conformational motion.



Naphthacene pillar

- correct spacing
- literature ?
- extension ?

AFOSR/CA V98 5

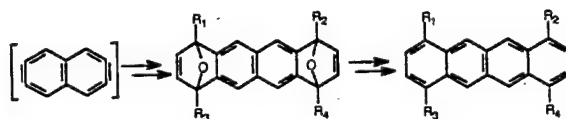
Research Plan

- Generation/synthesis of appropriate spacer
- Electrochemical characterization of spacer
- Porphyrin attachment/construction
- Electrochemical characterization of combo
- Alignment studies
- Optimization of spacer length

AFOSR/CA V98 6

10 Disubs. Naphthacenes

Bisbenzyne (Green) Approach

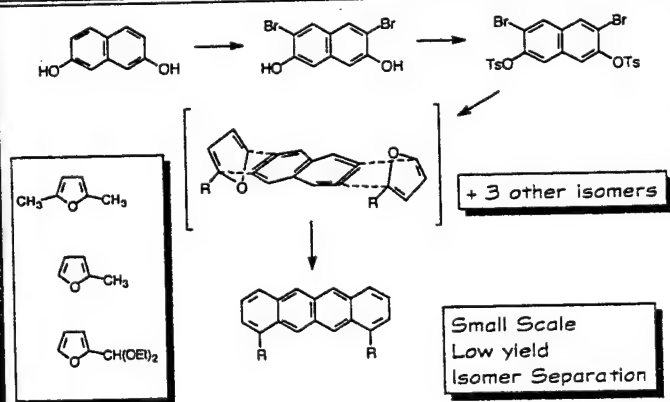


- Precursor synthesis simple
- Few steps
- ISOMERS

G.W. Gribble, R.B. Petti and K.D. Chan, *J.Org.Chem.*, 1985, 50, 2934.

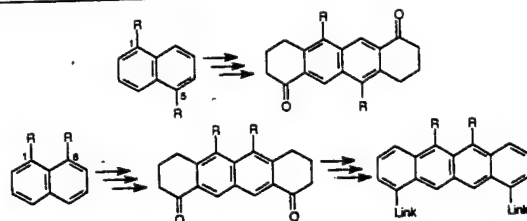
AFOSR/CA 1987

Bisbenzyne (Green) Approach



AFOSR/CA 1988

Annulation Approach

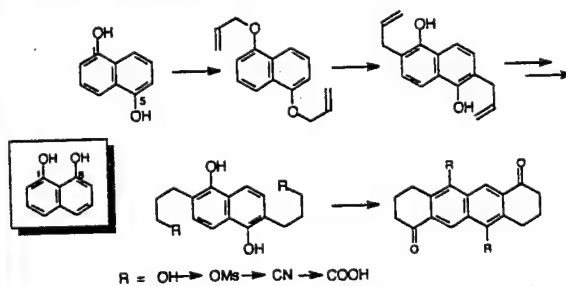


- Precursor synthesis needs to be addressed
- Multiple steps
- No ISOMERS
- Spacer stability

I. Takahashi, A. Nomura and H. Kurojima, *Synth. Comm.*, 1990, 20(10), 1569.

AFOSR/CA V98 9

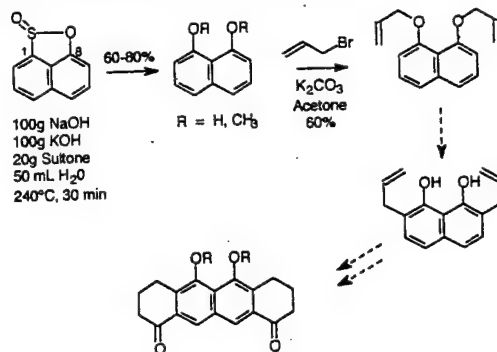
Reported Annulation Sequence



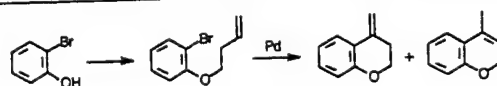
a) N.G. Anderson, S.P. Maddaford and B.A. Keay, *J.Org.Chem.*, 1996, 61, 9556; b) A.P. Lurie, G.H. Brown, J.R. Thimle and A.J. Weissberger, *J.Am.Chem.Soc.*, 1961, 83, 5015; F. Hibbert and K. Spears, *J.Chem.Soc., Perkin Trans. 2*, 1988, 571; N.G. Anderson, personal communication.

AFOSR/CA V98 10

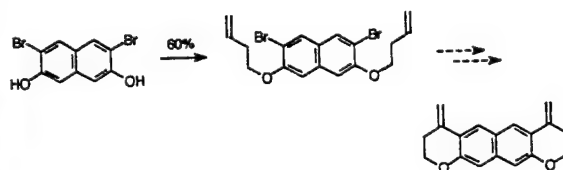
Current Annulation Sequence



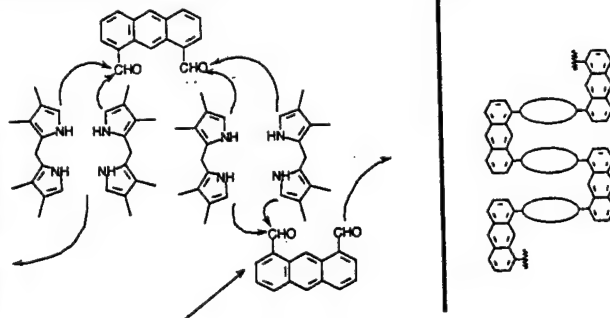
New Annulation Sequence



R.F. Heck, et al., J. Org. Chem., 1983, 48, 3894.



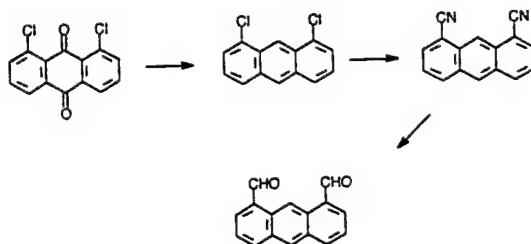
"Polymeric" Porphyrin Assembly



L. Abdalmuhdi and C.K. Chang, *J.Org.Chem.*, 1985, 50, 411,
T. Nagata, A. Osuka and K. Maruyama, *J.Am.Chem.Soc.*, 1989, 112, 3054.

APOS/CA 1988 13

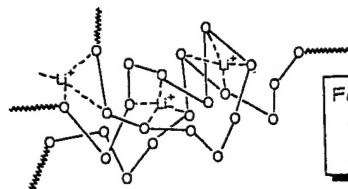
1,8-Anthracenedialdehyde



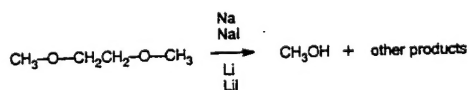
M.E. Rogers and B.A. Avenit, *J.Org.Chem.*, 1986, 51, 3308.

APOS/CA 1988 14

IR Project / GC/MS Project



Formation of precipitate at electrode(s)
PEO Decomposition?

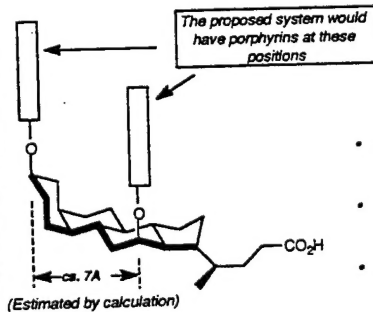


FTIR
Absorption at $\sim 1100 \text{ cm}^{-1}$
No absorption found ??

GC/MS
MeOH Found
Larger PEO Model

AFOSR/CA 1998 15

"Molecular Tweezers" Approach

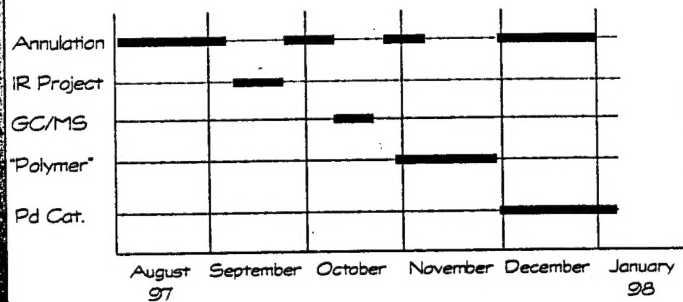


- Saturated framework
- Spacer length OK
- Available naturally

L. D'Souza and Uday Maitra, J.Org.Chem., 1996, 61, 9494.

AFOSR/CA 1998 16

Project Time Line



AFOSR/CA 1998 17

Acknowledgements

- Postdoctoral Associate - Dr. Denise Weimers
- Dr. Larry Scanlon, POOS CON, WPAFB
- NCEE - F33615-94-C-2419
- AFOSR - F49620-97-1-0169

AFOSR/CA 1998 18

Subject: Re: F49620-97-1-0157

Date: Thu, 03 Sep 1998 07:41:21 -0400 (EDT)

From: Arnab Shaw <ashaw@cs.wright.edu>

To: Jackie Frederick <jafreder@wright.edu>

Jackie:

No, no particular patent or invention to report, this was mainly developmental work.

Thanks.

--arnab

On Thu, 3 Sep 1998, Jackie Frederick wrote:

> *Date: Thu, 03 Sep 1998 07:38:23 -0400*

> *From: Jackie Frederick <jafreder@wright.edu>*

> *To: ashaw@cs.wright.edu,*
 jafreder@wright.edu

> *Subject: F49620-97-1-0157*

>

> *Dr. Shaw:*

>

> *We need to submit a final patent report on the above grant on your*

> *account #663442. Please advise if you have any inventions you need to*
> *report on this form.*

>

> *Thanks,*

>

> *Jackie Frederick*

> *Research & Sponsored Programs*

>

>

Arnab Kumar Shaw
Assoc. Prof., Elect. Engg. Dept.
Wright State University
Dayton, Ohio 45435, USA

Phone : (937)-775-5064
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FAX**Date** 08/28/98**Number of pages including cover sheet** 2**TO:** Leon Testas
Wright State University**Phone** 937-775-2425**Fax Phone** 937-775-3781**FROM:** Joyce Burch/PKA
Air Force Office of
Scientific Research
110 Duncan Ave
Bolling AFB, DC 20332-
8050**Email:** joyce.burch@afosr.af.mil**Phone** 202-767-6836**Fax Phone** 202-404-7951**CC:****REMARKS:** ☐ Urgent ☐ For your review ☒ Reply ASAP ☐ Please Comment

Mr Testas:

Attached is a listing of all delinquent reports for Wright State Univ that AFOSR has. I'm working on the next option for Prof Gilkey's grant F49620-97-1-0231 and we need to receive his delinquent reports in order to award the next option come beginning of the fiscal year. All reports need to be submitted as soon as possible.

Thank you for your help.

Joyce Burch
Contract Specialist